# VAN DER WAALS EQUATION OF STATE

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problems 5.48 - 5.51.

The *van derWaals model* of a substance is able to predict (qualitatively) the existence of the liquid-gas phase transition and the critical point (where there is no clear distinction between the liquid and gas phases). Schroeder gives a good explanation of the van der Waals model in section 5.3 of his book so I won't go over the whole thing here, but it's worth stating the main points.

The model is a refinement of the ideal gas equation of state, $PV = NkT$, which looks like this:

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = NkT \tag{1}$$

where $a$ and $b$ are constants whose values depend on the particular substance we're describing. The correction to the volume term is due to the fact that in a real substance, it is not possible to reduce the volume to zero since the molecules have a size below which they cannot be compressed further. Thus the minimum volume of a system of $N$ molecules is $Nb$, where $b$ depends on the nature of the substance.

The correction to the pressure is obtained from the following argument. Due to electric interactions, all molecules exhibit a long term attraction to each other. The potential energy due to the interaction between one molecule and its neighbours depends on the density of molecules $N/V$; a higher density means that a given molecule has more neighbours, and thus a higher potential energy due to electrical interactions. The total potential energy of the whole system due to these interactions is then proportional to the number $N$ of molecules times the potential energy per molecule, which is $-aN^2/V$, where $a$ is the constant of proportionality, which depends on the substance. [The potential energy is negative since we're dealing with an attractive interaction. Thus two molecules separated by some finite distance require positive work done on them to pull them apart to an infinite distance, at which point the potential energy is zero. That is, the work is required to pull them out of a potential well, so their potential energy is negative.]

The effect of this on the pressure can be obtained from the thermodynamic identity $dU = T\, dS - P\, dV$. If we consider a system in which all

the molecules are frozen in place then the entropy will not change. Increasing the volume of this system by $dV$ will reduce the potential energy by an amount $dU$ (since the neighbours will be further apart), so that

$$dU = -P\,dV \tag{2}$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_S \tag{3}$$

$$= -\frac{\partial}{\partial V}\left[-\frac{aN^2}{V}\right] \tag{4}$$

$$= -a\frac{N^2}{V^2} \tag{5}$$

Thus the attractive interaction produces a *negative* correction to the overall pressure, as we would expect (if the molecules are mutually attracted to each other, this pulls them together and reduces the pressure they exert on their container. The net pressure therefore becomes

$$P = \frac{NkT}{V - Nb} - a\frac{N^2}{V^2} \tag{6}$$

which gives the van der Walls equation 1.

To get a feel for the model, we can plot some isotherms on a $PV$ diagram:
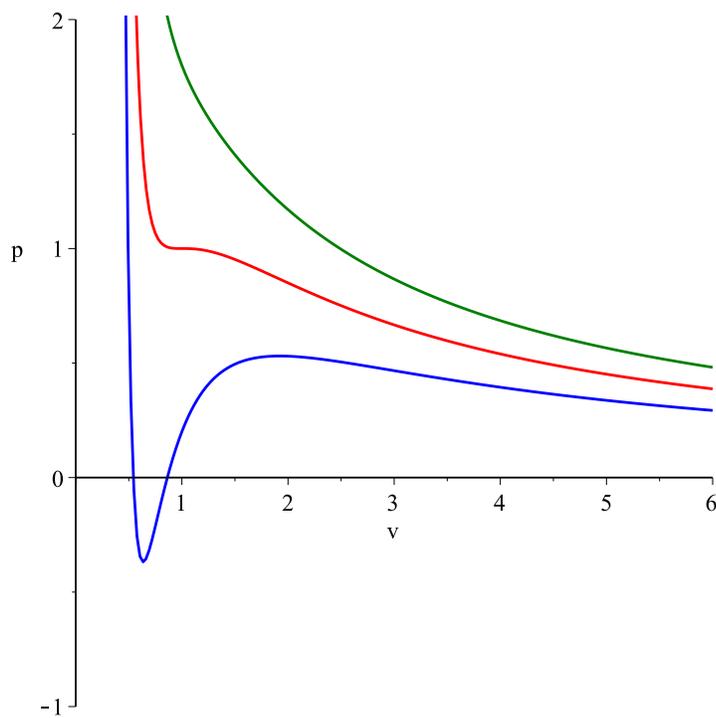
[These are actually plots of $p \equiv P/P_c$ versus $v \equiv V/V_c$ where the critical pressure $P_c$ and volume $V_c$ will be defined in a minute (see 17 below). At this point, we're interested only in the shapes of the curves.] The blue curve is for a temperature $0.8T_c$ (where the critical temperature $T_c$ will also be defined in a minute; have patience!), the red curve is for $T_c$ and the green curve is for $1.2T_c$. For $T < T_c$, the curve shows a minimum pressure as we reduce the volume, which seems to indicate that as we compress the substance, its pressure actually *decreases*. The red curve shows that at the critical temperature $T = T_c$, the minimum in the pressure curve becomes an inflection point, where both $\frac{dP}{dV}$ and $\frac{d^2P}{dV^2}$ are zero (this is a point like that in the graph of $y = x^3$ at $x = 0$). As we increase $T$ above $T_c$, the minimum in the pressure disappears and we are left with a curve that gets closer to that for an ideal gas, where $P = NkT/V$ (which is a hyperbola).

So does the van der Waals model actually predict a decrease in pressure as we compress the substance? The answer is 'no' as we can see if we examine the Gibbs free energy. Schroeder gives a complete description of how this works, which I won't repeat here. However, it's worth looking at one more graph to see what actually happens. We'll examine the blue curve (for $T = 0.8T_c$) above in a bit more detail:
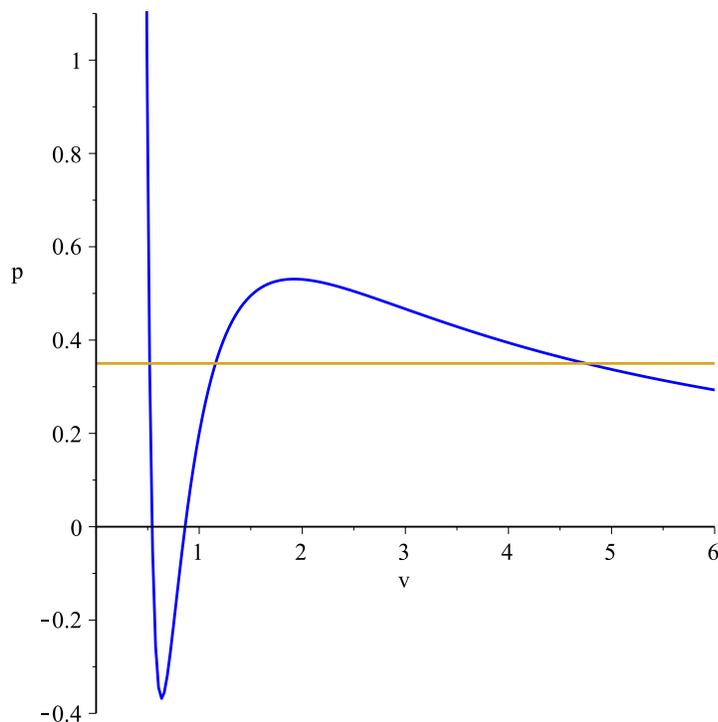


Suppose we follow the yellow horizontal line from right to left. Look first at the right-most intersection between the line and the blue curve, at

around $v = 4.8$. At this point, the substance is a gas. According to the van der Waals equation, this same pressure is also obtained when the volume is around $v = 1.1$, and again when the volume has decreased to about $v = 0.5$. However, if we look at the Gibbs energies for these three points, we find that the Gibbs energy is the same for $v = 0.5$ as it is for $v = 4.8$, but that the Gibbs energy for the point $v = 1.1$ is *higher* than the other two points. In other words, when the pressure is that given by the yellow line, the system will be found either at $v = 4.8$ *or* at $v = 0.5$ but *not* at $v = 1.1$, since the latter state is unstable. That is, there are two stable states at that pressure and temperature: a high-volume state (a gas) and a low-volume state (a liquid).

The critical point occurs at the lowest temperature for which there is only a single intersection between a horizontal line and the $PV$ curve, which occurs when the curve has an inflection point, as is shown by the red curve in the first graph above. We can find this by taking the first two derivatives of $P$ in 6 and setting them to zero:

$$\frac{\partial P}{\partial V} = -\frac{NkT}{(V - Nb)^2} + \frac{2aN^2}{V^3} = 0 \tag{7}$$

$$\frac{\partial^2 P}{\partial V^2} = \frac{2NkT}{(V - Nb)^3} - \frac{6aN^2}{V^4} = 0 \tag{8}$$

We can solve these 2 equations for $V$ and $T$:

$$T = 2aN\frac{(V - Nb)^2}{kV^3} \tag{9}$$

$$0 = \frac{4aN^2}{(V - Nb)V^3} - \frac{6aN^2}{V^4} \tag{10}$$

$$V_c = 3Nb \tag{11}$$

$$T_c = \frac{8}{27}\frac{a}{bk} \tag{12}$$

Substituting these back into 6 gives $P_c$:

$$P_c = \frac{a}{27b^2} \tag{13}$$

We can rewrite the van der Waals equation 6 in terms of dimensionless reduced variables $v \equiv V/V_c$, $t \equiv T/T_c$ and $p \equiv P/P_c$. We get

$$V = 3Nbv \tag{14}$$

$$T = \frac{8}{27}\frac{a}{bk}t \tag{15}$$

$$P = \frac{a}{27b^2}p \tag{16}$$

Making these substitutions and simplifying, we get

$$p = \frac{8tv^2 - 9v + 3}{(3v - 1)\,v^2} \tag{17}$$

which is conveniently independent of $a$ and $b$. It is this equation that was used to generate the plots above.

Using the critical parameters above, we can calculate the *compression factor* of the fluid at its critical point. The compression factor is defined as the ratio $PV/NkT$ and since this is 1 for an ideal gas, its actual value can be used as a measure of how much the fluid differs from an ideal gas. Plugging in the critical values above, we find

$$\frac{P_c V_c}{NkT_c} = \frac{3}{8} = 0.375 \tag{18}$$

As Schroeder points out, the compression factors of real fluids at their critical points are usually lower than this. Water, for example, has a compression factor of 0.227.

Finally, we can work out the critical parameters for a few substances, assuming that the van der Waals model is accurate for them (which it probably isn't). Rather than use Schroeder's values for $a$ and $b$, I'll use these from Wikipedia. The values for $a$ are given in strange units ($L^2 \cdot bar \cdot mol^{-2}$) where the L stands for 'litre'. To convert these to $J \cdot m^3$ for a single molecule, we divide by $10N_A^2$. The values for $b$ are given in L·mol$^{-1}$; to convert this to m$^3$, divide by $1000N_A$.

| | $a$ $\left(J\cdot m^3\right)$ | $b$ $\left(m^3\right)$ | $T_c$ (K) | $P_c$ (bar) | $\frac{V_c}{N}$ $\left(m^3\right)$ |
|---|---|---|---|---|---|
| $N_2$ | $3.78 \times 10^{-49}$ | $6.43 \times 10^{-29}$ | 126.2 | 33.9 | $1.93 \times 10^{-28}$ |
| $H_2O$ | $1.53 \times 10^{-48}$ | $5.06 \times 10^{-29}$ | 649.2 | 221 | $1.58 \times 10^{-28}$ |
| He | $9.55 \times 10^{-51}$ | $3.95 \times 10^{-29}$ | 5.19 | 2.27 | $1.19 \times 10^{-28}$ |

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